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Docket No.: 220759US0PCT

COMMISSIONER FOR PATENTS  
ALEXANDRIA, VIRGINIA 22313

RE: Application Serial No.: 10/069,983

Applicants: Florence L'ALLORET

Filing Date: March 14, 2002

For: FOAMING EMULSIONS AND FOAMING  
COMPOSITIONS CONTAINING A POLYMER  
COMPRISING WATER-SOLUBLE UNITS AND  
UNITS WITH AN LCST, ESPECIALLY FOR  
COSMETIC USES

Group Art Unit: 1713

Examiner: Egwin, K.

SIR:

Attached hereto for filing are the following papers:

**Appeal Brief w/Malcolm and Rowlinson Publication (1957); and Dow Corning Technical Sheet:  
propylene glycols" attached**

Our credit card payment form in the amount of **\$500.00** is attached covering any required fees. In the event any variance exists between the amount enclosed and the Patent Office charges for filing the above-noted documents, including any fees required under 37 C.F.R. 1.136 for any necessary Extension of Time to make the filing of the attached documents timely, please charge or credit the difference to our Deposit Account No. 15-0030. Further, if these papers are not considered timely filed, then a petition is hereby made under 37 C.F.R. 1.136 for the necessary extension of time. A duplicate copy of this sheet is enclosed.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.

Norman F. Oblon

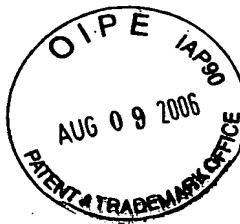
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DOCKET NO: 220759US0PCT



IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF

FLORENCE L'ALLORET

: EXAMINER: EGWIM, K.

SERIAL NO: 10/069,983

:

FILED: MARCH 14, 2002

: GROUP ART UNIT: 1713

FOR: FOAMING EMULSIONS AND  
FOAMING COMPOSITIONS  
CONTAINING A POLYMER  
COMPRISING WATER-SOLUBLE UNITS  
AND UNITS WITH AN LCST,  
ESPECIALLY FOR COSMETIC USES

**APPEAL BRIEF**

COMMISSIONER FOR PATENTS  
ALEXANDRIA, VIRGINIA 22313

SIR:

This brief is submitted in response to the rejections dated March 10, 2006.

**REAL PARTY OF INTEREST**

The real party of interest herein is L'Oréal of Paris, France.

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**RELATED APPEALS AND INTERFERENCES**

An Appeal has been filed in related application serial no. 10/069,981. This related application is being examined by the same Examiner and contains similar rejections as those outlined below.

**STATUS OF CLAIMS**

Claims 44-49 and 104-148 are active in this application.

Claims 47-49, 105-109, 111-115, 117, 1118, 120-124, 127-130, 132, 133, 137-142 and 145-148 have been withdrawn in view of the Office's restriction requirement.

Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, 143 and 144 are rejected.

**STATUS OF AMENDMENTS**

There are no outstanding amendments in this case.

**SUMMARY OF CLAIMED SUBJECT MATTER**

The invention currently under examination is to a method of lowering the surface tension or the interface tension of water by adding a polymer to the water in an amount sufficient to achieve this effect.

The polymer comprises water-soluble units and units with an LCST, the units with an LCST having in water a demixing temperature of from 5 to 40 °C at a concentration of 1% by mass in water, the polymer comprises an oligomer or copolymer of water-soluble units, and wherein the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l.

As discussed in the specification on page 4, lines 16-25, the invention is based on the discovery that certain polymers meeting this definition have the advantageous property of lowering the surface tension or the interface tension of water and as such particular useful for manufacturing foaming compositions and emulsions. This discovery significantly advances the state of the art, because it enables one to make such foaming compositions and emulsions with smaller amounts of typical emulsifiers and foaming agents (such as surfactants, which have a relatively aggressive negative affect on the skin (see pages 6-7 of the present specification). Compositions made using these polymers remain stable over a wide temperature range which is a property that is particularly useful in consumer cosmetic products which have to be maintained in various temperatures (e.g., manufacturing, shipping, and storage in a retail store.

In the Examples section of the application, various polymers were prepared that are representative of the claimed invention. In particular as outlined in Table 1 on page 37 of the specification, for example, polymers having polyacrylic acid backbones were used to graft on units with LCST  $(EO)_6(PO)_{39}$  (polymer 1) and poly-N-isopropyl-acrylamide (polymer 2).

As described in Example 1 beginning on page 43 through page 45, including Table 3, the surface tensions effects of polymers 1 and 2 upon addition to water were assessed. The measurements were performed at two temperatures, 15°C and 38°C; and compared to the polyacrylic backbone by itself, the  $(EO)_6(PO)_{39}$  graft by itself, or the poly-N-isopropyl-acrylamide graft by itself. The results are depicted in Table 3 and summarized on page 45, last paragraph: The results of Table 3 show that a significant reduction in the surface tension of water is obtained with polymers 1 and 2, this reduction being even greater above the demixing temperature.

**ISSUES TO BE REVIEWED ON APPEAL**

- (1) The first issue to be reviewed on appeal is the rejection Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136 and 143-144 under 35 U.S.C. § 112, first paragraph based on the allegation that the claims include new matter.
- (2) The second issue to be reviewed on appeal is the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 as being anticipated by U.S. patent no. 4,767,265 (“Merchant”)
- (3) The third issue to be reviewed on appeal is the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 as being anticipated by U.S. patent no. 4,839,167 (“Yamamoto”).
- (4) The fourth issue to be reviewed on appeal is the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 as being anticipated by U.S. patent no. 5,338,352 (“Breneman”).
- (5) The fifth issue to be reviewed on appeal is the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 as being anticipated by JP 61245835 (“Ezaki”)
- (6) The sixth issue to be reviewed on appeal is the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 as being anticipated by U.S. patent no. 4,274,977 (“Koerner”).
- (7) The seventh issue to be reviewed on appeal is the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 as being anticipated by U.S. patent no. 4,559,226 (“Fogel”).
- (8) The eighth issue to be reviewed on appeal is the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 as being anticipated by EP 1055694 (“Yabuta”).

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(9) The ninth issue to be reviewed on appeal is the rejection of Claims 44-46, 104, 110, 116, 119, 125, 126, 131, 134-136, and 143-144 as being anticipated by EP 583814 or EP629649 ("the Maroy publications")

There remains an obviousness-type double patenting rejection in view of copending application serial no. 10/069,981. However, as this case is still pending, review of this rejection is not requested at this time.

## ARGUMENTS

### Summary of the Argument

There are fundamental differences between the claimed method, i.e., the polymer employed, and those polymers used in the cited prior art references. Specifically, unlike the polymer defined in the claims, the polymers described in the cited prior art exhibited a cloud point (in other words, the polymers of the prior art are NOT water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l). The art relied upon by the Examiner in the rejections does not describe such polymers, does not lead one to select such polymers, and, in fact, the Examiner has simply failed to provide factual basis to support the rejections.

In maintaining the prior art rejections (which are all clumped together), the Examiner contends that “it is noted that the features upon which applicant relies (i.e., wherein the polymer does not exhibit an LCST or does not have cloud points) are not recited in the rejected claim(s).” (page 4 of the final Office Action of March 10, 2006). It is respectfully submitted that this is an allegation without merit. Specifically, the claims specifically require that the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l, which as one knows means that within the temperature range cited in the claims, the polymer does not exhibit a cloud point or LCST. This fact, which the Examiner has seemingly failed to appreciate, differentiates the claimed invention from the descriptions provided in the prior art.

It is well-settled law that the standard set forth in § 102(b) is that of novelty. Lack of novelty, i.e., anticipation requires strict identity between the claimed invention and that disclosed in the prior art reference. To anticipate a claim, a single prior art source must contain all of the essential limitations of the claim *Verdegaal Bros. v. Union Oil Co. of California* 2 USPQ2d 1051, 1053 (Fed. Cir. 1987). Put very simply, the claimed invention is

not described by the cited art with sufficient specificity as to constitute anticipation under U.S. patent law and therefore the rejections under 35 U.S.C. § 102(b) should be REVERSED.

Issue #1

The Examiner contends that the specification does not support the limitation that "the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l" and specifically does not find support for the phrase on pages 4-5 of the specification. It is respectfully submitted that the specification unquestionably provides adequate written description to apprise one in this field that the inventors had possession of the claimed invention. In particular, the specification clearly describes that at a concentration of 0.1% by mass (i.e., 10 g/l) the polymer remains soluble in the water at a temperature from 5 to 80°C because it can lower the surface tension or interface tension of the water. As one can appreciate, if the polymer is not soluble in the water at this temperature, it would not cause such an effect. In addition, the specification supports the claims at page 2, lines 23-27 in relation to page 2, lines 2-8; page 6, lines 30-33, page 7, lines 10-11; and page 8, lines 32-35.

Further in support of the patentability of the claimed invention, Appellants note that the Board of Patent Appeals and Interferences has overturned a rejection made under 35 U.S.C. § 112, first paragraph where the Examiner rejected claims on the grounds that the claim expressions did not appear in the original disclosure (In re Sorenson 3 USPQ2d 1462 (BPAI 1987) - copy attached for convenience). In this case, the terms "binuclear copper complexes of carboxylic acids", "binuclear copper complex of an aliphatic carboxylic acid" and "a binuclear copper complex of an arylcarboxylic acid" were held not to violate 35 U.S.C. § 112, first paragraph in view of the fact that the specification contained four examples of binuclear cooper complexes of carboxylic acids and one example of a binuclear

copper complex of an aliphatic carboxylic acid. "Given those working examples together with a broader disclosure of copper complexes of carboxylic acids, both aliphatic and aromatic, we have no doubt that the Applicants' disclosure *reasonably conveys to the skilled artisan that Appellant had possession of the subject matter now claimed.*" Id. at 1464 (italics added). In dicta the BPAI stated "we are mindful that Appellants' specification need not describe the claimed invention in *ipsis verbis* to comply with a written description requirement" Id. at 1463, and "the test is whether the originally filed specification disclosure *reasonably conveys to a person having ordinary skill that Applicant had possession of the subject matter later claimed.*" Id. at 1464 citing to In re Kaslow 217 U.S.P.Q. 1089 (CAFC 1983).

The decision in Sorenson is relevant to the present rejection and support the claimed phrase that is rejected by the Examiner. Therefore, the present claims does not represent new matter and was described in the original specification in such a way as to reasonably convey to one of ordinary skill in the art that the inventors had possession of the claimed invention.

Issue # 2

Merchant does not describe, with any specificity, the polymer employed in the claimed method. In fact, assessment of the polymers Merchant does disclose would lead one to different polymers.

The polymers disclosed in Merchant do not contain an oligomer or copolymer of water-soluble units as claimed (see the maleic anhydride grafted to an alkyl phenol formaldehyde resin in col. 6, lines 41-49), and the polymers disclosed in Merchant do not contain LCST units, which are one of the limitations that defines the claims over this reference—see the p-nonyl phenyl formaldehyde resin having 10 moles of ethylene oxide in the Examples of Merchant (see col. 10, lines 42-45 and col. 11, lines 29-30).

This formaldehyde resin with 10 moles of ethylene oxide contained in the polymers are not LCST units as has been clearly shown in the Malcolm and Rowlinson publication, now of record. What becomes clear from this publication is that the Merchant polymers described are those that have no LCST. In this Malcolm publication, Figure 6 (Page 926) shows the phase diagrams for polyethylene oxide (indicated in squares and crosses) in which above the curve there exists two phases, below the curve there exists one phase, and the lowest point of the curve defines the LCST. Therefore, this Figure shows that as the molecular weight of the polyethylene oxide gets smaller, the two phase domain also gets smaller. Also illustrated is that for a POE of 3000, the two phase domain is indicated as the oval in the Figure. Taken together then, 10 units of polyethylene oxide as is the case in Merchant would only exhibit 1 phase, i.e., no LCST.

In maintaining this rejection previously, the Examiner has stated that the teachings of the reference are not as limited as the examples illustrated in the above-discussion. The point is missed. The point here is that the species specifically exemplified by Merchant are exemplary of Merchant's emulsifiers and are simply not the same polymers as defined in the

claimed method and that absent such a description, Merchant does not provide the requisite disclosure to select monomers of water-soluble and LCST units and arrange them in the manner that would be the same as the polymer defined in the claimed method. Using the language from MPEP 2131.02, one of ordinary skill in the art would not be able to "at once envisage" the polymers set forth in the claimed method.

Moreover, Merchant does not describe the arrangement set forth in dependent Claim 104, in which the polymer is either

- (1) water-soluble units alternating with units with an LCST; or
- (2) a graft polymer whose backbone is formed from water-soluble units and bears LCST grafts.

In fact, the Office has failed to provide any reasons why this claim has been rejected in view of Merchant.

Moreover, Merchant does not describe or provide any suggestion for providing the arrangement in Claim 116, wherein water-soluble units have a molar mass ranging from 1000 g/mol to 5 000 000 g/mol when they constitute the water-soluble backbone of a grafted polymer, or a molar mass ranging from 500 g/mol to 100 000 g/mol when they constitute a block of a multiblock polymer or when they constitute the grafts of a grafted polymer. In fact, the Office has failed to provide any reasons why this claim has been rejected in view of Merchant.

In view of this, the claims cannot be anticipated by the Merchant disclosure.

Issue #3

Yamamoto describes hair care products with an emulsion containing a hair fixative polymer which is water soluble (col. 2, line 10-23 and col. 3, lines 45-46) and can be one of several polymers listed in col. 3, lines 51-63 none of which are the types of polymers claimed. In response to the Office's comment on page 4 of the Official Action, it is stressed that just because Yamamoto may disclose a particular monomer that may have LCST properties (referring to the statement on page 4 of the Office Action of March 3, 2005 concerning vinylpyrrolidone), there is insufficient disclosure that permits one to envision the types of polymers used in the claimed method. That is, Yamamoto does not describe in any manner, polymers having an oligomer or copolymer of water-soluble units, LCST units with specified properties such that the polymer, as a whole, is water-soluble in the temperature and concentration ranges set forth in the claims.

It should be noted that the Office has already recognized these differences in the related co-pending application, US serial no. 10/069,981, by withdrawing the rejection based on Yamamoto in view of many of the same elements of the polymer as claimed herein. The Office has not provided any additional reasons why this rejection remains in this case, nor in the final office action, are there any reasons whatsoever as to why this rejection has been maintained.

Issue #4

Breneman fails to describe with any specificity polymers meeting the definition of the polymer set forth in the claimed method.

The polymers that Brenemann describes are organomodified silicone emulsifiers (col. 2, line 13) in which heating and agitation are required to form an oil-in-water emulsion (col. 3, lines 34-35). Breneman also describes a polyether modified polysiloxane, which is a copolymer of hydrophilic and hydrophobic monomers. The fact that the polymers in Breneman are not the same is missed by the Office—see conclusion set forth on page 4 of the Office Action mailed March 3, 2005 (i.e., “the water-soluble units and the LCST units are one in the same”). The Brenemann polymers do not contain water-soluble units and the specific types of LCST units in the polymer having all of the features as set forth in the claims—oligomer or copolymer of water-soluble units, and water soluble within defined temperature and concentration ranges.

Again it should be noted that the Office has already recognized these differences in the related co-pending application, US serial no. 10/069,981, by withdrawing the rejection based on Brenemann in view of many of the same elements of the polymer as claimed herein. The Office has not provided any additional reasons why this rejection remains in this case, nor in the final office action, are there any reasons whatsoever as to why this rejection has been maintained.

Issue #5

Ezaki describes a nonionic surfactant with a specific cloud point: see “Purpose” on page 1 “To stably dissolve an emulsion in water without receiving the effect of the temp. of dissolving water, by adding a nonionic surfactant **having a specific cloud point** to a water . . .” See also “Constitution” “. . .nonionic surfactant polyethylene glycol type one) having a cloud point of . . .”

Ezaki does not describe any polymer as required in the present claims, having water-soluble and LCST units, comprises an oligomer or copolymer of water-soluble units, and which is water-soluble within specified temperature and concentrations ranges. The Office has provided no specific reasons or specific explanation as to why this rejection has been maintained.

Issue #6

Koerner describes an alkyl polyether at the top of col. 8, which polymer has a cloud point, i.e., the polymer exhibits an LCST, at a specific temperature and concentration (col. 8, lines 1-6). This polymer, however, is different from the polymer defined in the claims where the polymer is water-soluble in a specified range and concentration (see Claim 44).

Moreover, the polymers described elsewhere in Koerner, e.g., columns 5 and 6, also have a cloud point (see col. 6, lines 24-29) and thus are not the same as the polymer defined in the claimed dispersion.

In maintaining the rejection in the final Office Action, the Office proffers no explanation as to why the claims have been continually rejected over this reference. In a previous Office Action of June 29, 2005, the rejection based on Koerner was maintained, at least in part, because “the particular polymer of example 8 has a cloud point at a higher concentration than the concentration recited in the claims.” (Page 4 of the Official Action) However, as is quite apparent that the polymers used in the claimed method do not have a cloud point or LCST (i.e., are water-soluble within a specified concentration and temperature ranges) and distinguishes the claims from the description provided by Koerner.

**Issue #7**

The polymers of Fogel have a cloud point, which clearly makes those polymers different from the polymers used in the claimed method (i.e., are water-soluble within a specified concentration and temperature ranges).

In maintaining the rejection in the final Office Action, the Office proffers no explanation as to why the claims have been continually rejected over this reference. In a previous Office Action of June 29, 2005, the Office stated: "applicant appears to be ignoring the polyoxyethylene portions of the water-soluble polymers, i.e., wherein y is from 1 to 20."

This disclosure in Fogel was not ignored and moreover, is not particularly relevant to the claimed invention. These polyoxyethylene portions are the water-soluble portion of the alkoxylate esters. Said another way, the  $-(OCH_2CH_2)$  is the water-soluble portion and  $(R_2)_x$  is the LCST portion of the alkoxylate ester.

Specifically, the alkoylate ester of a specific formula where  $R_2$  can be either (a) or (b) and  $x$  is from 1 to 10 (see col. 2, lines 53-62) are those having cloud points within the range that the claimed polymers are to be water-soluble. The technical basis for this distinction is reiterated below.

Polyoxypropylene groups, e.g., when  $x$  is 10, have a molecular weight of 580 g/mol and have a demixing temperature, i.e., cloud point, at a 1% concentration of 65°C (see P600E) (Dow Corning Technical Sheet: polypropylene glycol—of record). Furthermore, where  $x$  is less than 10, the demixing temperature, i.e., cloud point, is much greater than 65°C (see, e.g., P400E). Therefore, the polymers in Fogel are unquestionably different from the polymer defined in the claims

**Issue #8**

Yabuta describes a block copolymer of ethylene glycol and propylene glycol, which polymer has a cloud point, i.e., the polymer exhibits an LCST, in the 30 to 90°C range (see [0096] and [0097] on page 11). This polymer, however, is different from the polymer defined in the claims where the polymer does not exhibit an LCST and remains soluble in water (i.e., see Claim 44: “water-soluble within a specified concentration and temperature ranges”).

In maintaining the rejection in the final Office Action, the Office proffers no explanation as to why the claims have been continually rejected over this reference. The previous explanations as to the differences between the claims and Yabuta were also not specifically addressed in the final Office Action.

As explained above, the claims define the manner in which the polymers do not have an LCST, i.e., are water soluble within defined temperature and concentration ranges. As the polymers disclosed by Yabuta have cloud points within this range, this means that they are not water-soluble in the manner as required for the polymers used in the claimed methods.

Issue #9

The Maroy publications are acknowledged and discussed on page 1, lines 24-25 and page 2, lines 10-14 of the present specification, noting that documents [4] and [5] are the Maroy publications. The Maroy publications describe a polymer with water-soluble groups and LCST groups (page 2, lines 26-30 of EP '814). Maroy also describes that the groups with LCST can be copolymerized with the water-soluble groups or grafted onto a hydrosoluble skeleton (page 2, lines 34-44 of EP '814).

Maroy does not describe a polymer containing LCST units having a demixing temperature of 5 to 40°C at 1% by mass in water in the claimed method nor provide any description that would lead one to the polymers that are water-soluble in a temperature and concentration as set forth in the claims under active consideration. In fact, the LCST units described in the Maroy publications do NOT have, in water, a demixing temperature of from 5 to 40°C at 1% by mass in water. Specifically, on page 2, lines 53-56 and page 3, lines 2-3 of EP '814 and col. 2, line 54 to col. 3, line 4, Maroy describes that the LCST units selected from polyethyleneglycol (POE), polyoxypropylene (POP) or polyoxide of ethylene and propylene (POEP). Furthermore, Examples 1.1, 1.2, 1.3, and 1.4 of EP '814 (Maroy) on pages 3-4, all describe polymers with POE5 as the LCST units, which is polyethyleneglycol with a molecular weight of 5000 g/mol. However, these polymers have a demixing temperature above 100°C at a concentration of 1 % by mass (see page 5, line 41, page 6, lines 37-39, and page 6, lines 57-59 of EP '814). Therefore, these polymers cannot be the same as the polymer defined in the claimed dispersion (having a demixing temperature of 5 to 40°C at 1% by mass in water).

In Example 2.3 (page 7) of EP '814 (Maroy), the polymer contains POP of a molecular weight of 600 as the LCST unit. However, unlike the polymer in the claimed dispersion, this polymer of Maroy has a demixing temperature of 48°C at a concentration of 1

% by mass. In Example 2.5 (pages 7-8) of EP '814 (Maroy), the polymer contains a POEP polymer with a molecular weight of approximately 1100. However, unlike the polymer in the claims, this polymer has a demixing temperature above 60°C (see Figure 3 of EP '814).

In the Examples of EP '649, Maroy describes the same example as 1.2 from EP '814 (see the reference to French application 9210224, which is the priority application of EP '814 in col. 6, line 40 and lines 54-56) and Examples 4 and 5 which include POE with a molecular weight of about 5000. For the same reasons as discussed above concerning EP '814, these specifically described polymers have a demixing temperature above 60°C and are therefore NOT the same as the polymer set forth in the claims.

In maintaining the rejection in the final Office Action, the Office proffers no explanation as to why the claims have been continually rejected over this reference. In a previous Office Action of June 29, 2005, it is stated that "the Examiner fails to find any specific teachings of demixing temperatures above 40°C at 1% by mass in water as suggested by applicant. However, it is reasonable that the LCST units of Maroy et al., would possess the presently claimed properties since the LCST units are identical to applicants." Applicants disagree and have already provided evidence of the differences.

In summary, uncontested evidence has been provided that clearly shows the polymers described by the Maroy publications do not necessarily, each and every time, have the properties of the polymer defined in the claimed method. The Office has simply maintained the rejections providing no specific reasons or any evidence that contradicts the evidence provided.

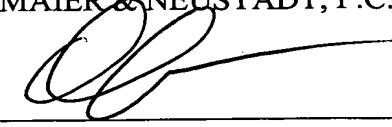
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Appeal Brief

**CONCLUSION**

In view of the above remarks, Appellants request that all of the rejections be  
REVERSED.

Respectfully submitted,

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APPENDIX 1 (CLAIMS)

Claims 1-43 (Cancelled).

44. (Previously Presented) A method of lowering the surface tension or the interface tension of water comprising adding a polymer comprising water-soluble units and units with an LCST, the units with an LCST having in water a demixing temperature of from 5 to 40 °C at a concentration of 1% by mass in water, to water in an amount sufficient to lower the surface tension or the interface tension of water, wherein the polymer comprises an oligomer or copolymer of water-soluble units, and wherein the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l.

45. (Previously Presented) The method as claimed in claim 44, in which the lowering of the surface tension or of the interface tension of water is at least 15 mN/m for a concentration of polymer in water of 0.1% by mass in the temperature range from 5 to 80 °C.

46. (Previously Presented) The method as claimed in claim 44, in which the lowering of the surface tension or of the interface tension of water is of at least 20 mN/m for a concentration of polymer in water of 0.1% by mass when the temperature is higher than the demixing temperature of the units with an LCST at this concentration.

47. (Withdrawn) A method of manufacturing a foam, comprising mixing a polymer comprising water-soluble units and units with an LCST, the units with an LCST having in water a demixing temperature of from 5 to 40 °C at a concentration of 1% by mass in water with water; and generating a foam, the polymer comprises an oligomer or copolymer of water-soluble units, and wherein the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l.

48. (Withdrawn) The method as claimed in Claim 47, further comprising mixing a foaming surfactant at a concentration of less than or equal to 5% by mass.

49. (Withdrawn) A method of manufacturing an emulsion, comprising mixing a polymer comprising water-soluble units and units with an LCST, the units with an LCST having in water a demixing temperature of from 5 to 40 C at a concentration of 1% by mass in water, with water and at least one oil; and generating the emulsion, wherein the emulsion is free of additional emulsifying surfactant or comprises an additional emulsifying surfactant at a concentration of less than or equal to 1% by mass, the polymer comprises an oligomer or copolymer of water-soluble units, and wherein the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l.

Claims 50-103 (Cancelled).

104. (Previously Presented) The method as claimed in Claim 44, wherein the polymer is in the form of a block polymer comprising water-soluble units alternating with units with an LCST, or in the form of a grafted polymer whose backbone is formed from water-soluble units and which bears grafts consisting of units with an LCST or a grafted polymer whose backbone is formed from units with an LCST and which bears grafts consisting of water-soluble units.

105. (Withdrawn) The method as claimed in Claim 104, wherein the polymer is partially crosslinked.

106. (Withdrawn) The method as claimed in Claim 47, wherein the polymer is in the form of a block polymer comprising water-soluble units alternating with units with an LCST, or in the form of a grafted polymer whose backbone is formed from water-soluble units and which bears grafts consisting of units with an LCST or a grafted polymer whose backbone is formed from units with an LCST and which bears grafts consisting of water-soluble units.

107. (Withdrawn) The method as claimed in Claim 106, wherein the polymer is partially crosslinked.

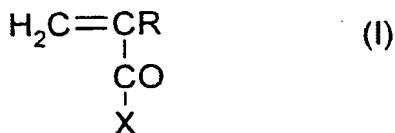
108. (Withdrawn) The method as claimed in Claim 49, wherein the polymer is in the form of a block polymer comprising water-soluble units alternating with units with an LCST, or in the form of a grafted polymer whose backbone is formed from water-soluble units and which bears grafts consisting of units with an LCST or a grafted polymer whose backbone is formed from units with an LCST and which bears grafts consisting of water-soluble units.

109. (Withdrawn) The method as claimed in Claim 108, wherein the polymer is partially crosslinked.

110. (Previously Presented) The method as claimed in Claim 44, wherein the water-soluble units are obtained by free-radical polymerization of at least one monomer selected from the group consisting of:

(meth)acrylic acid;

vinyl monomers of formula (I) below:



wherein:

R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula

$N^+R_1R_2R_3$  wherein  $R_1$ ,  $R_2$  and  $R_3$  are, independently, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of  $R^+ + R_1 + R_2 + R_3$  does not exceed 7; and

- $NH_2$ ,  $-NHR_4$  and  $-NR_4R_5$  groups in which  $R_4$  and  $R_5$  are, independently of each other, linear or branched, saturated or unsaturated hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in  $R_4 + R_5$  does not exceed 7, the said  $R_4$  and  $R_5$  optionally being substituted with a halogen atom (iodine, bromine, chlorine or fluorine); a hydroxyl (-OH); sulphonic ( $-SO_3^-$ ), sulphate ( $-SO_4^-$ ); phosphate ( $-PO_4H_2$ ); primary amine ( $-NH_2$ ); secondary amine ( $-NHR_1$ ), tertiary amine ( $-NR_1R_2$ ) and/or quaternary amine ( $-N^+R_1R_2R_3$ ) group with  $R_1$ ,  $R_2$  and  $R_3$  being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of  $R_4 + R_5 + R_1 + R_2 + R_3$  does not exceed 7;

maleic anhydride;

itaconic acid;

vinyl alcohol of formula  $CH_2=CHOH$ ;

vinyl acetate of formula  $CH_2=CH-OCOCH_3$ ;

$N$ -vinyllactams such as  $N$ -vinylpyrrolidone,  $N$ -vinylcaprolactam and  $N$ -butyrolactam;

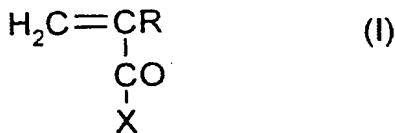
vinyl ethers of formula  $CH_2=CHOR_6$  in which  $R_6$  is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms;

water-soluble styrene derivatives, especially styrene sulphonate; dimethyldiallylammonium chloride; and vinylacetamide.

111. (Withdrawn) The method as claimed in Claim 47, wherein the water-soluble units are obtained by free-radical polymerization of at least one monomer selected from the group consisting of:

(meth)acrylic acid;

vinyl monomers of formula (I) below:



wherein:

R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub> wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are, independently, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> does not exceed 7; and

-NH<sub>2</sub>, -NHR<sub>4</sub> and -NR<sub>4</sub>R<sub>5</sub> groups in which R<sub>4</sub> and R<sub>5</sub> are, independently of each other, linear or branched, saturated or unsaturated

hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in  $R_4 + R_5$  does not exceed 7, the said  $R_4$  and  $R_5$  optionally being substituted with a halogen atom (iodine, bromine, chlorine or fluorine); a hydroxyl (-OH); sulphonic ( $-SO_3^-$ ), sulphate ( $-SO_4^-$ ); phosphate ( $-PO_4H_2$ ); primary amine ( $-NH_2$ ); secondary amine ( $-NHR_1$ ), tertiary amine ( $-NR_1R_2$ ) and/or quaternary amine ( $-N^+R_1R_2R_3$ ) group with  $R_1$ ,  $R_2$  and  $R_3$  being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of  $R_4 + R_5 + R_1 + R_2 + R_3$  does not exceed 7;

maleic anhydride;

itaconic acid;

vinyl alcohol of formula  $CH_2=CHOH$ ;

vinyl acetate of formula  $CH_2=CH-OCOCH_3$ ;

N-vinylactams such as N-vinylpyrrolidone, N-vinylcaprolactam and N-butyrolactam;

vinyl ethers of formula  $CH_2=CHOR_6$  in which  $R_6$  is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms;

water-soluble styrene derivatives, especially styrene sulphonate;

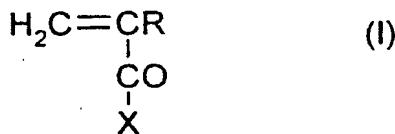
dimethyldiallylammonium chloride; and vinylacetamide.

112. (Withdrawn) The method as claimed in Claim 49, wherein the water-soluble units are obtained by free-radical polymerization of at least one monomer selected from the group consisting of:

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(meth)acrylic acid;

vinyl monomers of formula (I) below:



wherein:

R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub> wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are, independently, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> does not exceed 7; and

-NH<sub>2</sub>, -NHR<sub>4</sub> and -NR<sub>4</sub>R<sub>5</sub> groups in which R<sub>4</sub> and R<sub>5</sub> are, independently of each other, linear or branched, saturated or unsaturated hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in R<sub>4</sub> + R<sub>5</sub> does not exceed 7, the said R<sub>4</sub> and R<sub>5</sub> optionally being substituted with a halogen atom (iodine, bromine, chlorine or fluorine); a hydroxyl (-OH); sulphonic (-SO<sub>3</sub><sup>-</sup>), sulphate (-SO<sub>4</sub><sup>-</sup>); phosphate (-PO<sub>4</sub>H<sub>2</sub>); primary amine (-NH<sub>2</sub>); secondary amine (-NHR<sub>1</sub>),

tertiary amine (-NR<sub>1</sub>R<sub>2</sub>) and/or quaternary amine (-N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>) group with R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R<sub>4</sub> + R<sub>5</sub> + R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> does not exceed 7;

maleic anhydride;

itaconic acid;

vinyl alcohol of formula CH<sub>2</sub>=CHOH;

vinyl acetate of formula CH<sub>2</sub>=CH-OCOCH<sub>3</sub>;

N-vinyl lactams such as N-vinylpyrrolidone, N-vinylcaprolactam and N-butyrolactam;

vinyl ethers of formula CH<sub>2</sub>=CHOR<sub>6</sub> in which R<sub>6</sub> is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms;

water-soluble styrene derivatives, especially styrene sulphonate;

dimethyldiallylammonium chloride; and vinylacetamide.

113. (Withdrawn) The method as claimed in Clam 44, wherein the water-soluble units comprises one or more members selected from the group consisting of a water-soluble polyurethane, xanthan gum, alginate; alginate derivative; cellulose derivatives; galactomannan; galactomannan derivatives thereof; and polyethyleneimine.

114. (Withdrawn) The method as claimed in Clam 47, wherein the water-soluble units comprises one or more members selected from the group consisting of a water-soluble polyurethane, xanthan gum, alginate; alginate derivative; cellulose derivatives; galactomannan; galactomannan derivatives thereof; and polyethyleneimine.

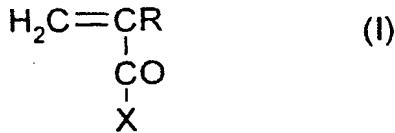
115. (Withdrawn) The method as claimed in Claim 49, wherein the water-soluble units comprises one or more members selected from the group consisting of a water-soluble polyurethane, xanthan gum, alginate; alginate derivative; cellulose derivatives; galactomannan; galactomannan derivatives thereof; and polyethyleneimine.

116. (Previously Presented) The method as claimed in Claim 44, wherein the water-soluble units have a molar mass ranging from 1000 g/mol to 5 000 000 g/mol when they constitute the water-soluble backbone of a grafted polymer, or a molar mass ranging from 500 g/mol to 100 000 g/mol when they constitute one block of a multiblock polymer or when they constitute the grafts of a grafted polymer.

117. (Withdrawn) The method as claimed in Claim 47, wherein the water-soluble units have a molar mass ranging from 1000 g/mol to 5 000 000 g/mol when they constitute the water-soluble backbone of a grafted polymer, or a molar mass ranging from 500 g/mol to 100 000 g/mol when they constitute one block of a multiblock polymer or when they constitute the grafts of a grafted polymer.

118. (Withdrawn) The method as claimed in Claim 49, wherein the water-soluble units have a molar mass ranging from 1000 g/mol to 5 000 000 g/mol when they constitute the water-soluble backbone of a grafted polymer, or a molar mass ranging from 500 g/mol to 100 000 g/mol when they constitute one block of a multiblock polymer or when they constitute the grafts of a grafted polymer.

119. (Previously Presented) The method as claimed in Claim 44, wherein the units with an LCST comprises one or more of the following:  
polyethers; polyvinyl methyl ethers; polymeric N-substituted acrylamide derivatives;  
and a vinyl monomer corresponding to formula (I):



wherein:

R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub> wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are, independently, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> does not exceed 7; and

-NH<sub>2</sub>, -NHR<sub>4</sub> and -NR<sub>4</sub>R<sub>5</sub> groups in which R<sub>4</sub> and R<sub>5</sub> are, independently of each other, linear or branched, saturated or unsaturated hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in R<sub>4</sub> + R<sub>5</sub> does not exceed 7, the said R<sub>4</sub> and R<sub>5</sub> optionally being substituted with a halogen atom (iodine, bromine, chlorine or fluorine); a hydroxyl (-OH); sulphonic (-SO<sub>3</sub><sup>-</sup>), sulphate (-SO<sub>4</sub><sup>2-</sup>); phosphate (-PO<sub>4</sub>H<sub>2</sub>); primary amine (-NH<sub>2</sub>); secondary amine (-NHR<sub>1</sub>), tertiary amine (-NR<sub>1</sub>R<sub>2</sub>) and/or quaternary amine (-N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>) group with R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms,

with the proviso that the sum of the carbon atoms of  $R_4 + R_5 + R_1 + R_2 + R_3$

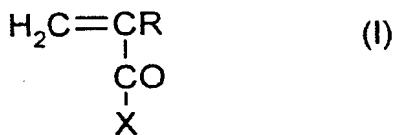
does not exceed 7;

a monomer selected from the group consisting of maleic anhydride, itaconic acid, vinylpyrrolidone, styrene and its derivatives, dimethyldiallylammonium chloride, vinylacetamide, vinyl ethers and vinyl acetate derivatives; or polyvinylcaprolactam; copolymers of vinylcaprolactam and a vinyl monomer corresponding to formula (I).

120. (Withdrawn) The method as claimed in Claim 47, wherein the units with an

LCST comprises one or more of the following:

polyethers; polyvinyl methyl ethers; polymeric N-substituted acrylamide derivatives; and a vinyl monomer corresponding to formula (I):



wherein:

R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

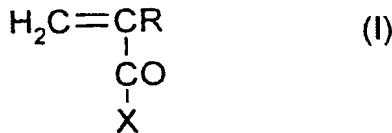
OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub> wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are, independently, a linear or branched,

saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of  $R' + R_1 + R_2 + R_3$  does not exceed 7; and

$-NH_2$ ,  $-NHR_4$  and  $-NR_4R_5$  groups in which  $R_4$  and  $R_5$  are, independently of each other, linear or branched, saturated or unsaturated hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in  $R_4 + R_5$  does not exceed 7, the said  $R_4$  and  $R_5$  optionally being substituted with a halogen atom (iodine, bromine, chlorine or fluorine); a hydroxyl (-OH); sulphonic ( $-SO_3^-$ ), sulphate ( $-SO_4^-$ ); phosphate ( $-PO_4H_2$ ); primary amine ( $-NH_2$ ); secondary amine ( $-NHR_1$ ), tertiary amine ( $-NR_1R_2$ ) and/or quaternary amine ( $-N^+R_1R_2R_3$ ) group with  $R_1$ ,  $R_2$  and  $R_3$  being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of  $R_4 + R_5 + R_1 + R_2 + R_3$  does not exceed 7;

a monomer selected from the group consisting of maleic anhydride, itaconic acid, vinylpyrrolidone, styrene and its derivatives, dimethyldiallylammonium chloride, vinylacetamide, vinyl ethers and vinyl acetate derivatives; or polyvinylcaprolactam; copolymers of vinylcaprolactam and a vinyl monomer corresponding to formula (I).

121. (Withdrawn) The method as claimed in Claim 49, wherein the units with an LCST comprises one or more of the following: polyethers; polyvinyl methyl ethers; polymeric N-substituted acrylamide derivatives; and a vinyl monomer corresponding to formula (I):



wherein:

R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub> wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are, independently, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> does not exceed 7; and

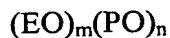
-NH<sub>2</sub>, -NHR<sub>4</sub> and -NR<sub>4</sub>R<sub>5</sub> groups in which R<sub>4</sub> and R<sub>5</sub> are, independently of each other, linear or branched, saturated or unsaturated hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in R<sub>4</sub> + R<sub>5</sub> does not exceed 7, the said R<sub>4</sub> and R<sub>5</sub> optionally being substituted with a halogen atom (iodine, bromine, chlorine or fluorine); a hydroxyl (-OH); sulphonic (-SO<sub>3</sub><sup>-</sup>), sulphate (-SO<sub>4</sub><sup>-</sup>); phosphate (-PO<sub>4</sub>H<sub>2</sub>); primary amine (-NH<sub>2</sub>); secondary amine (-NHR<sub>1</sub>), tertiary amine (-NR<sub>1</sub>R<sub>2</sub>) and/or quaternary amine (-N<sup>+</sup>R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>) group with R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> being, independently of each other, a linear or branched,

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saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of  $R_4 + R_5 + R_1 + R_2 + R_3$  does not exceed 7;

a monomer selected from the group consisting of maleic anhydride, itaconic acid, vinylpyrrolidone, styrene and its derivatives, dimethyldiallylammonium chloride, vinylacetamide, vinyl ethers and vinyl acetate derivatives; or polyvinylcaprolactam; copolymers of vinylcaprolactam and a vinyl monomer corresponding to formula (I).

122. (Withdrawn) The method as claimed in Claim 44, wherein the units with an LCST consist of polypropylene oxides of formula  $(PPO)_n$  with n being an integer from 10 to 50, or random copolymers of ethylene oxide (EO) and of propylene oxide (PO), represented by the formula:



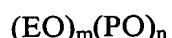
in which m is an integer of from 1 to 40 and n is an integer ranging from 10 to 60.

123. (Withdrawn) The method as claimed in Claim 47, wherein the units with an LCST consist of polypropylene oxides of formula  $(PPO)_n$  with n being an integer from 10 to 50, or random copolymers of ethylene oxide (EO) and of propylene oxide (PO), represented by the formula:



in which m is an integer of from 1 to 40 and n is an integer ranging from 10 to 60.

124. (Withdrawn) The method as claimed in Claim 44, wherein the units with an LCST consist of polypropylene oxides of formula  $(PPO)_n$  with n being an integer from 10 to 50, or random copolymers of ethylene oxide (EO) and of propylene oxide (PO), represented by the formula:



in which m is an integer of from 1 to 40 and n is an integer ranging from 10 to 60.

125. (Previously Presented) The method as claimed in Claim 44, wherein the molar mass of the units with an LCST is from 500 to 5300 g/mol.

126. (Previously Presented) The method as claimed in Claim 125, wherein the molar mass of the units with an LCST is from 1500 to 4000 g/mol.

127. (Withdrawn) The method as claimed in Claim 47, wherein the molar mass of the units with an LCST is from 500 to 5300 g/mol.

128. (Withdrawn) The method as claimed in Claim 127, wherein the molar mass of the units with an LCST is from 1500 to 4000 g/mol.

129 (Withdrawn) The method as claimed in Claim 49, wherein the molar mass of the units with an LCST is from 500 to 5300 g/mol.

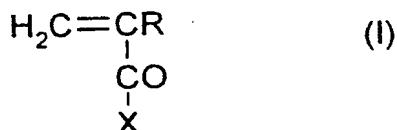
130. (Withdrawn) The method as claimed in Claim 129, wherein the molar mass of the units with an LCST is from 1500 to 4000 g/mol.

131. (Previously Presented) The method as claimed in Claim 44, wherein the units with an LCST comprise

a polyvinylcaprolactam;

a copolymer of vinylcaprolactam and of a vinyl monomer corresponding to formula

(I):



wherein:

R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula  $N^+R_1R_2R_3$  wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are, independently, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> does not exceed 7; or

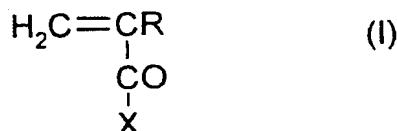
a monomer selected from the group consisting of maleic anhydride, itaconic acid, vinylpyrrolidone, styrene; styrene derivatives, dimethyldiallyl ammonium chloride, vinylacetamide, vinyl alcohol, vinyl acetate, vinyl ethers, and vinyl acetate derivatives.

132. (Withdrawn) The method as claimed in Claim 49, wherein the units with an LCST comprise

a polyvinylcaprolactam;

a copolymer of vinylcaprolactam and of a vinyl monomer corresponding to formula

(I):



wherein:

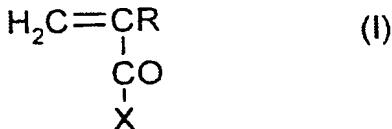
R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula  $N^+R_1R_2R_3$  wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are, independently, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> does not exceed 7; or

a monomer selected from the group consisting of maleic anhydride, itaconic acid, vinylpyrrolidone, styrene; styrene derivatives, dimethyldiallylammonium chloride, vinylacetamide, vinyl alcohol, vinyl acetate, vinyl ethers, and vinyl acetate derivatives.

133. (Withdrawn) The method as claimed in Claim 49, wherein the units with an LCST comprise  
a polyvinylcaprolactam;  
a copolymer of vinylcaprolactam and of a vinyl monomer corresponding to formula (I):



wherein:

R is from H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub> or -C<sub>3</sub>H<sub>7</sub>, and

X is:

OR' alkyl oxides wherein R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom; a sulphonic group, a sulphate group, a phosphate group; a hydroxyl group; a primary amine; a secondary amine; a tertiary amine; or a quaternary amine group of the formula  $N^+R_1R_2R_3$  wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are, independently, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R<sub>1</sub> + R<sub>2</sub> + R<sub>3</sub> does not exceed 7; or

a monomer selected from the group consisting of maleic anhydride, itaconic acid, vinylpyrrolidone, styrene; styrene derivatives, dimethyldiallylammonium chloride, vinylacetamide, vinyl alcohol, vinyl acetate, vinyl ethers, and vinyl acetate derivatives.

134. (Previously Presented) The method as claimed in Claim 44, wherein the proportion by mass of the units with an LCST is from 5 to 70% relative to the polymer.

135. (Previously Presented) The method as claimed in Claim 134, wherein the proportion by mass of the units with an LCST is from 20 to 65% relative to the polymer.

136. (Previously Presented) The method as claimed in Claim 134, wherein the proportion by mass of the units with an LCST is from 30 to 60% relative to the polymer.

137. (Withdrawn) The method as claimed in Claim 47, wherein the proportion by mass of the units with an LCST is from 5 to 70% relative to the polymer.

138. (Withdrawn) The method as claimed in Claim 137, wherein the proportion by mass of the units with an LCST is from 20 to 65% relative to the polymer.

139. (Withdrawn) The method as claimed in Claim 137, wherein the proportion by mass of the units with an LCST is from 30 to 60% relative to the polymer.

140. (Withdrawn) The method as claimed in Claim 49, wherein the proportion by mass of the units with an LCST is from 5 to 70% relative to the polymer.

141. (Withdrawn) The method as claimed in Claim 140, wherein the proportion by mass of the units with an LCST is from 20 to 65% relative to the polymer.

142. (Withdrawn) The method as claimed in Claim 140, wherein the proportion by mass of the units with an LCST is from 30 to 60% relative to the polymer.

143. (Previously Presented) The method as claimed in Claim 44, wherein the concentration by mass of the polymer in the aqueous phase is less than or equal to 5%.

144. (Previously Presented) The method as claimed in Claim 143, wherein the concentration by mass of the polymer in the aqueous phase is from 0.01% to 5%.

145. (Withdrawn) The method as claimed in Claim 47, wherein the concentration by mass of the polymer in the aqueous phase is less than or equal to 5%.

146. (Withdrawn) The method as claimed in Claim 145, wherein the concentration by mass of the polymer in the aqueous phase is from 0.01% to 5%.

147. (Withdrawn) The method as claimed in Claim 49, wherein the concentration by mass of the polymer in the aqueous phase is less than or equal to 5%.

148. (Withdrawn) The method as claimed in Claim 147, wherein the concentration by mass of the polymer in the aqueous phase is from 0.01% to 5%.

**APPENDIX II (EVIDENCE)**

The present specification as originally filed at page 4, lines 16-25.

The present specification as originally filed at pages 6-7.

The present specification as originally filed at page 37 including Table 1.

The present specification as originally filed at page 43 through page 45, including

Table 3.

Malcolm and Rowlinson publication (1957), entered into the record on May 25, 2005

Dow Corning Technical Sheet: Propylene glycol, entered into the record on May 25,

2005.

**RELATED PROCEEDINGS APPENDIX**

An appeal has been filed in U.S. application serial no. 10/069,981, a case that is related to the present application.

# THE THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL, POLYPROPYLENE GLYCOL AND DIOXANE

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Received 7th March, 1957

Measurements are reported of the vapour pressures, the heats of mixing, the densities and the phase relationships of solutions of polyethylene glycol and polypropylene glycol in water. The free energies, heats and entropies of dilution, the volume changes on mixing and the excess partial volumes have been derived. The results show significant differences from those for other polar polymer solutions. A comparison is made with the results for aqueous solutions of dioxane which is the cyclic dimer of the repeating unit in polyethylene glycol. Some new measurements of the vapour pressures of dioxane + water solutions at temperatures between 100° C and 156° C and of the heat of mixing at 25° C, are reported in an appendix.

Few precise measurements have yet been made of the thermodynamic properties of polymer solutions which contain polar molecules. This paper reports the results of a detailed investigation of the properties of the solutions of polyethylene glycol and polypropylene glycol in water. These solutions provide examples of polymer solutions in which association and clustering of solvent molecules may occur and in which orientation-dependent interactions are present between solvent and polymer. Polyethylene glycol and polypropylene glycol were chosen because they are the simplest available polyethers. Several other polyethers are in course of preparation for future study.

## EXPERIMENTAL

**MATERIALS.**—Samples of polyethylene and polypropylene glycols were kindly supplied by Oxirane Ltd. of Manchester. The number average molecular weights were given as 5000, 3000, 1500 and 300 for the polyethylene glycols and 750 and 400 for the polypropylene glycols. The solid samples were purified before use by reprecipitation with hexane from hot carbon tetrachloride solution. All the samples were carefully dried under high vacuum.

**VAPOUR PRESSURE MEASUREMENTS.**—The difference between the vapour pressure of the solution and that of pure water at the same temperature was measured with a mercury manometer in an apparatus similar to that used by Taylor and Rowlinson.<sup>1</sup> Times of up to 36 h were necessary for the pressure differences to become steady. The constancy of the thermostat was  $\pm 0.01$  deg. at 25° C and  $\pm 0.04$  deg. at 65° C. The thermometers were calibrated against thermometers standardized by the N.P.L. A correction for the vapour space was applied when calculating the concentrations. Measurements of the vapour pressure of water made with this apparatus agreed well with those recommended by Dorsey.<sup>2</sup>

**HEAT OF MIXING MEASUREMENTS.**—These were performed in an isothermal naphthalene calorimeter, which was a much enlarged version of the instrument described by Beynon and Humphries.<sup>3</sup> The central tube of the calorimeter was made 2 in. wide and 20 in. long. The lower 6 in. of this tube were separated from the rest by an evacuated B 55 ground glass stopper. A thin central tube through the stopper allowed two nylon threads to pass to the mixing vessel inside the reaction chamber. Two additional heat reflecting

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shields were added to those described by Beynon and Humphries. One of these was an aluminium foil sheet placed on the bottom face of the glass stopper. The other was a polished brass disc which was fixed immediately above the stopper and was heated electrically to maintain it at the temperature of the thermostat.

The mixing vessel, shown in fig. 1, was a glass sphere of 4 cm diameter divided into two compartments by an inner tube and a layer of mercury. When solid polymer material was used it was placed in the outer compartment, O, melted, solidified and weighed. Mercury was added completely to fill the outer compartment, and the requisite amount of water was then added to the inner compartment, I, from a weight burette. Liquid polymer material was placed on top of mercury in the outer compartment by means of a hypodermic syringe, and the water was then added as before. The vessel was closed by means of a tightly fitting rubber bung so that no vapour space remained. The bung was initially inserted well inside the vessel so that the slight expansion of the contents which occurred on heating up to 80° C was taken up by allowing the bung to be driven upwards until it pressed against a strong wire fastened round the vessel. Mixing and stirring were achieved by repeatedly tipping the vessel upside down by means of the nylon threads. The movement of the mercury served both to stir the solution and also to conduct the heat of mixing rapidly to the outer wall of the vessel. From there the heat was conducted by a silicone oil to the wall of the naphthalene chamber. (The level of the oil in the reaction chamber was always below the top of the naphthalene chamber.) The movement of the mercury in the capillary was measured with a cathetometer.

The sensitivity of the calorimeter was  $1.544 \pm 0.007 \text{ cm}^3/\text{cal}$  ( $1 \text{ cal} = 4.1840 \text{ joules}$ ). This figure gave a value of  $0.00429 \text{ cm}^3/\text{cal}$  for the volume change of naphthalene on fusion, which agreed well with the values  $0.00427$  and  $0.00433 \text{ cm}^3/\text{cal}$  recorded by Benyon and Humphries for their work and that of Coffin.<sup>4</sup> The apparatus was placed in a bath which could be maintained at constant temperature to within  $\pm 0.001^\circ \text{C}$  for periods of several hours. During an experiment variations in the rate of background drift of the mercury in the capillary tube were not more than  $0.001 \text{ cm/sec}$ . In each experiment amounts of the order of 1 to 6 g of each substance were used, and were chosen so that between 20 and 40 cal were evolved on mixing (except in the regions of extreme dilution or concentration). The time of a complete mixing experiment was usually 90 min, so that the maximum error which could be caused by change in the rate of background drift was 0.6%.

**DENSITY MEASUREMENTS.**—The densities of the solutions were measured in a bi-capillary pyknometer, which was filled by means of a hypodermic syringe. The pyknometer was calibrated at each temperature with distilled water.

**PHASE SEPARATION MEASUREMENTS.**—These were carried out by heating the solutions in Pyrex tubes. Each tube contained a short length of glass rod to aid stirring, and after filling with solution, was frozen, evacuated and sealed off. Heating up to  $250^\circ \text{C}$  was carried out in an oil bath. The temperature of incipient phase separation was first noted as the bath was slowly warmed (or cooled), and was compared with the temperature at which the solution first became clear again. Readings up to  $150^\circ \text{C}$  could be reproduced to within  $\pm 0.1^\circ \text{C}$ , those up to  $200^\circ \text{C}$  to  $\pm 1^\circ \text{C}$  and above  $200^\circ \text{C}$  to  $\pm 2^\circ \text{C}$ .

## RESULTS

### VAPOUR PRESSURE MEASUREMENTS

The vapour pressures and the solvent activities as functions of the polymer weight fraction are shown in tables 1 and 2.

The experimental error in the measured pressure differences is thought to be within  $\pm 1\%$ , and the error in the weight fractions is less than this amount. The vapour pressure values for water used in the calculation of the activities are those recommended by Dorsey.<sup>2</sup> Correction for the imperfection of the vapour was made using the equation of state of Keyes, Smith and Gerry.<sup>2</sup>

For all four solutions the vapour pressure isotherms are everywhere convex towards the vapour pressure axis. In this respect they differ from the isotherms for the nitro-cellulose + ketone systems<sup>5</sup> and the agar-agar + water system,<sup>6</sup> which have sigmoid

shapes. The vapour pressure curves were not dependent on whether the water concentration was being increased or decreased; that is, there was no hysteresis.

TABLE 1.—THE VAPOUR PRESSURES IN mm Hg (AT 0° C) OF AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL

temp. °C	wt. fraction of polymer ( $W_2$ )	vapour pressure ( $p_1$ )	activity of solvent ( $a_1$ )	wt. fraction of polymer ( $W_2$ )	vapour pressure ( $p_1$ )	activity of solvent ( $a_1$ )
<b>MOLECULAR WEIGHT 5000</b>						
65.00	0.990	35.71	0.191	0.835	150.73	0.805
	0.970	78.92	0.422	0.764	160.58	0.857
	0.951	102.31	0.547	0.735	165.62	0.884
	0.949	103.24	0.552	0.662	171.30	0.914
	0.902	132.48	0.708	0.496	182.79	0.974
	0.900	133.11	0.711	0.000	187.54	1.000
	0.839	150.33	0.803			
60.00	0.950	81.50	0.547	0.735	130.91	0.877
	0.902	104.22	0.699	0.000	149.38	1.000
	0.835	118.70	0.796			
<b>MOLECULAR WEIGHT 3000</b>						
65.00	0.990	34.36	0.184	0.846	145.01	0.774
	0.970	75.03	0.402	0.765	158.70	0.847
	0.950	99.26	0.531	0.704	166.34	0.888
	0.904	127.01	0.679	0.499	181.72	0.969
	0.897	130.46	0.697	0.000	187.54	1.000
55.00	0.970	47.10	0.400	0.702	102.62	0.871
	0.950	61.74	0.524	0.499	113.76	0.964
	0.844	89.45	0.759	0.000	118.04	1.000
<b>MOLECULAR WEIGHT 300</b>						
65.00	0.988	24.97	0.134	0.662	156.12	0.833
	0.951	63.95	0.342	0.489	173.54	0.926
	0.900	97.13	0.520	0.299	181.89	0.970
	0.801	132.31	0.707	0.000	187.54	1.000
50.00	0.988	12.12	0.132	0.660	75.58	0.818
	0.950	30.31	0.329	0.488	84.77	0.917
	0.899	46.07	0.499	0.298	89.39	0.966
	0.800	63.11	0.683	0.000	92.51	1.000
30.00	0.988	3.95	0.124	0.659	25.10	0.789
	0.950	9.81	0.309	0.488	28.65	0.900
	0.899	14.88	0.468	0.298	30.41	0.956
	0.800	20.61	0.648	0.000	31.82	1.000

TABLE 2.—THE VAPOUR PRESSURE IN mm Hg (AT 0° C) OF AQUEOUS SOLUTIONS OF POLYPROPYLENE GLYCOL 400

temp. °C	wt. fraction of polymer ( $W_2$ )	vapour pressure ( $p_1$ )	activity of solvent ( $a_1$ )	wt. fraction of polymer ( $W_2$ )	vapour pressure ( $p_1$ )	activity of solvent ( $a_1$ )
50.00	0.990	19.90	0.216	0.701	90.99	0.984
	0.952	59.13	0.640	0.591	91.68	0.991
	0.902	78.94	0.854	0.000	92.51	1.000
	0.801	89.05	0.963			
30.00	0.990	6.62	0.208	0.700	31.12	0.978
	0.950	19.88	0.625	0.590	31.36	0.985
	0.901	26.89	0.845	0.000	31.82	1.000
	0.800	30.40	0.955			

## CALOMETRIC MEASUREMENTS

The heat of mixing results are recorded in table 3.

TABLE 3.—THE HEATS OF MIXING AT 80.3° C FOR AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL IN cal/g OF MIXTURE AS A FUNCTION OF THE WEIGHT FRACTION OF POLYMER ( $W_2$ )

$W_2$	$-\Delta H$ cal/g	$W_2$	$-\Delta H$ cal/g
MOLECULAR WEIGHT 5000			
0.206	4.79	0.755	4.89
0.336	7.03	0.825	3.25
0.480	8.20	0.887	1.39
0.548	7.91	0.953	0.30
0.675	6.18		
MOLECULAR WEIGHT 3000			
0.102	2.32	0.780	4.66
0.303	6.59	0.847	2.87
0.517	8.14	0.904	1.33
0.719	5.92		
MOLECULAR WEIGHT 300			
0.287	6.29	0.820	5.26
0.475	8.05	0.897	3.10
0.630	7.44	0.948	1.42
0.719	6.59		

The probable error in the heat of mixing per gram of mixture is  $\pm 2\%$ . A comparison between these results and those for the dioxane + water system (see appendix) is made in fig. 2.

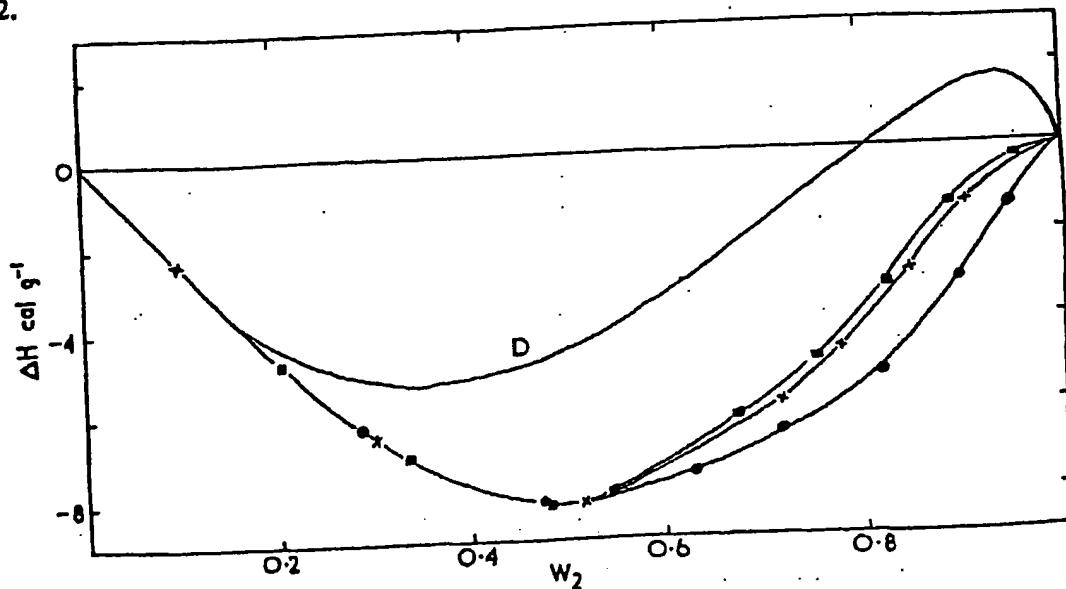


FIG. 2.—Heats of mixing at 80.3° C of polyethylene glycol and water plotted against weight fraction of polymer. Squares, mol. wt. 5000; crosses, mol. wt. 3000; circles, mol. wt. 300. Curve D, dioxane and water (20° C).

## THERMODYNAMIC DILUTION FUNCTIONS

The results in tables 1-3 were used to calculate free energies and heats of dilution for the four solutions. For the three polyethylene glycol solutions the free energies of dilution at 65° C and the heats of dilution at 80.3° C were combined to give approximate values of the entropies of dilution. (The heats of dilution calculated at several temperatures from the vapour pressure measurements indicate that the temperature coefficient of the heat of dilution is small and positive.) For the polypropylene glycol solutions the heats of dilution were calculated from the vapour pressure measurements, and are the mean

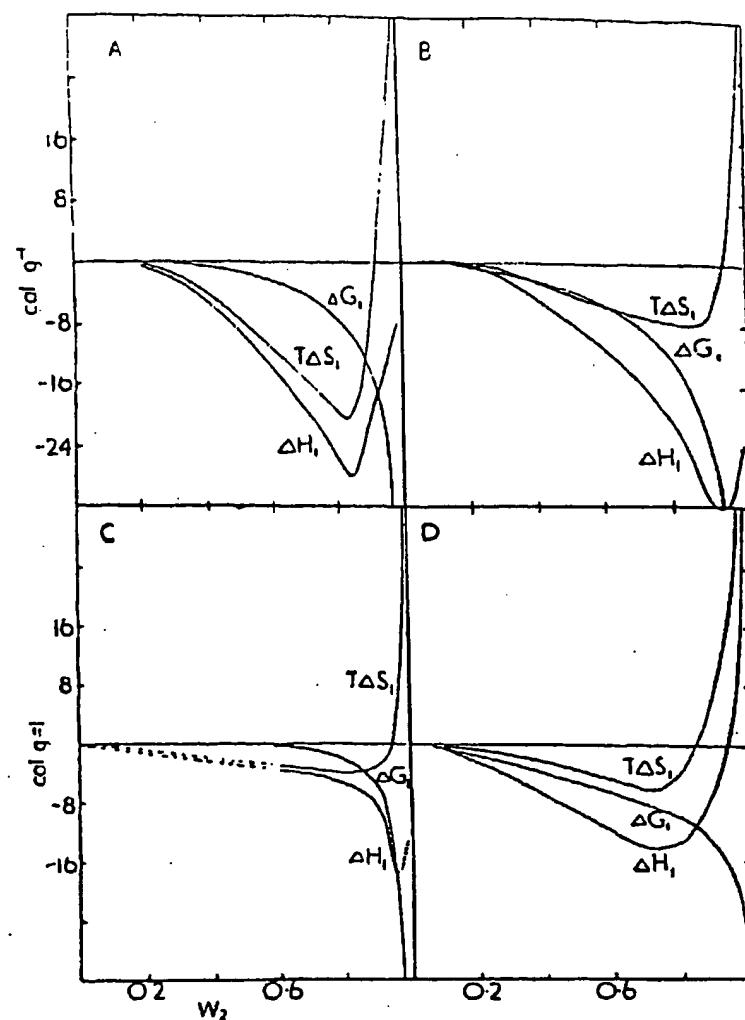


FIG. 3.—Thermodynamic dilution functions plotted against weight fraction of polymer or dioxane (see text). A and B, polyethylene glycols 5000 and 300; C, polypropylene glycol 400; D, dioxane.

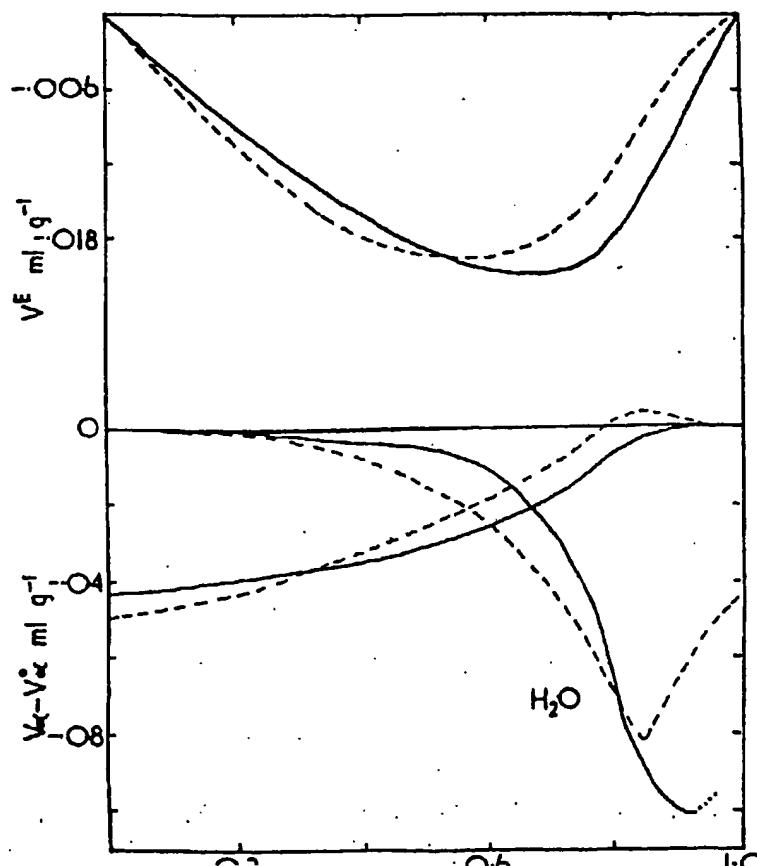


FIG. 4.—Excess volumes and excess partial volumes as functions of weight fraction of polymer or dioxane. Full lines, polyethylene glycol 5000 at 65°C; broken lines, dioxane at 25°C.

## SOLUTION OF POLYETHYLENE GLYCOL

values between 30° C and 50° C. The smoothed values of the three dilution functions are plotted in fig. 3. Fig. 3(D) shows the dilution functions for the dioxane + water system calculated from vapour pressures at 25° C and heats of mixing at 20° C (see appendix). The curves for the solution of polyethylene glycol 3000 are very similar to those for the sample of molecular weight 5000, and are not plotted in the figure.

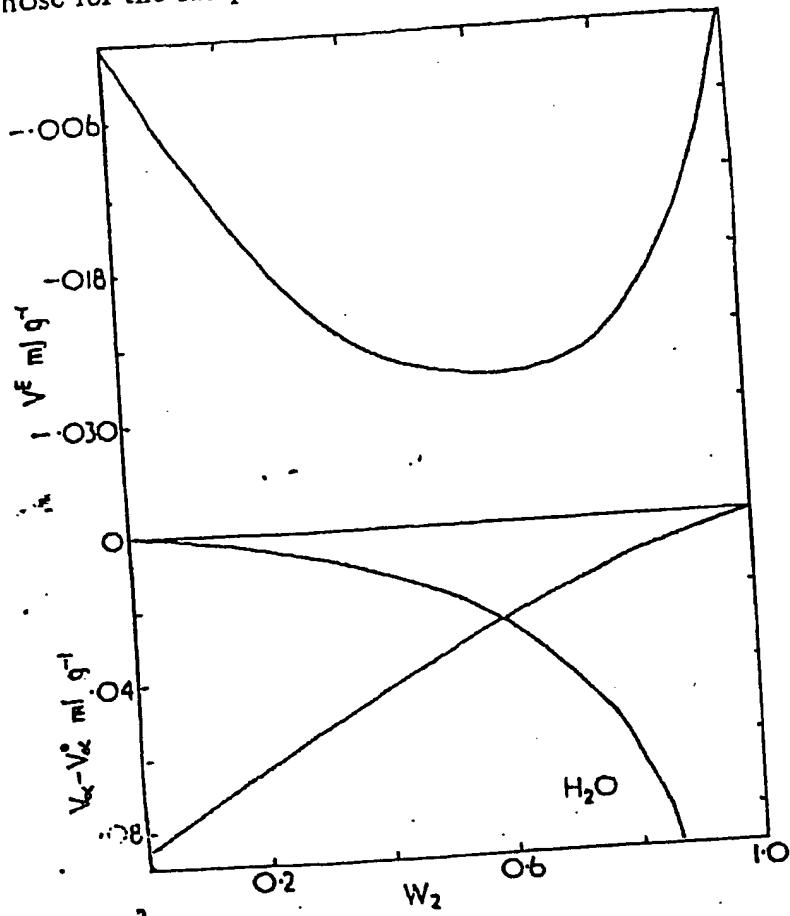


FIG. 5.—Excess volumes and excess partial volumes in solutions of polypropylene glycol 400 at 50° C as functions of the weight fraction of polymer.

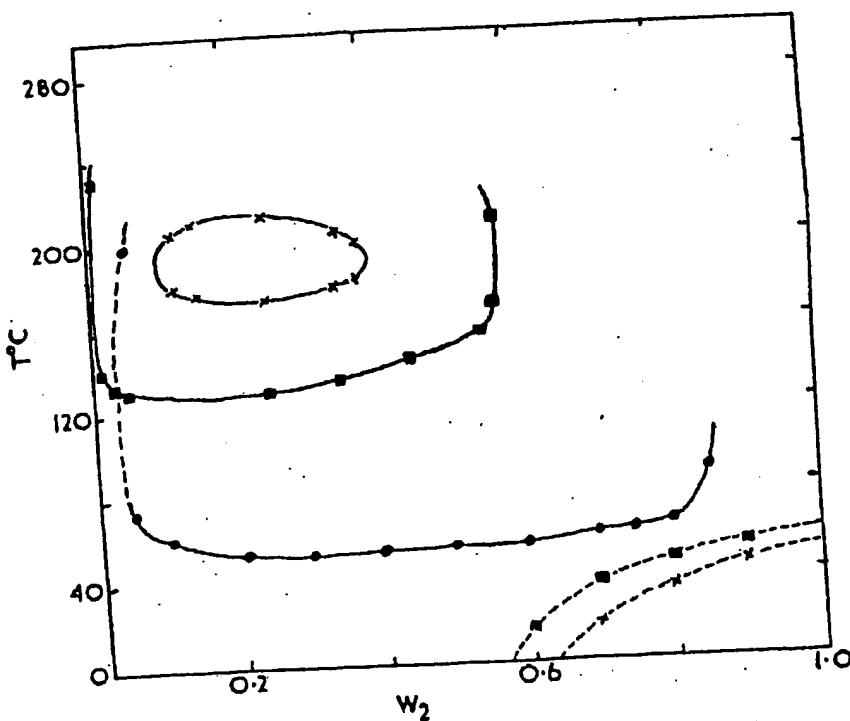


FIG. 6.—Phase diagram for aqueous solutions of polyethylene and polypropylene glycols. Squares and crosses, polyethylene glycols 5000 and 3000; circles, polypropylene glycol 400. Lower right-hand curves, solid-liquid boundaries.

## VOLUME CHANGES ON MIXING

The densities of the solutions of the three polyethylene glycols plotted against composition fell on the same smooth curve. The results were used to calculate the excess volumes of the components. These functions

are plotted in fig. 4, together with the corresponding results for the dioxane + water solution (see appendix). The results for the polypropylene glycol solutions are shown in fig. 5.

#### PHASE RELATIONSHIPS

The phase diagrams which were obtained are shown in fig. 6. No phase separation was observed in the solutions of polyethylene glycol 300 or dioxane.

#### DISCUSSION

Analysis of the results for the solution of polyethylene glycol 5000 in terms of the free energy equation

$$\Delta G_1 = RT\{\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2\} \quad (1)$$

gives values of the parameter  $\chi$  which increase uniformly with volume fraction of polymer ( $\phi_2$ ) from 0.4 at  $\phi_2 = 0.25$  to 0.75 at  $\phi_2 = 0.66$ , and then increase more rapidly to 1.24 at  $\phi_2 = 0.9$ .

For the nitrocellulose + ketone systems and the agar-agar + water solution the values of  $\chi$  decreased with increase in  $\phi_2$  and were negative at high concentrations of polymer. This difference in behaviour is further illustrated by the fact that the vapour pressure isotherms of the solutions studied here are not sigmoid in shape like those of the nitrocellulose and agar-agar solutions.

Examination of the thermodynamic dilution functions is interesting in this connection. For the solution of polyethylene glycol 5000 the excess of the entropy and heat of dilution over the values predicted by the equations,

$$\Delta S_1 = -R\{\ln(1 - \phi_2) + \phi_2\}, \quad (2)$$

and

$$\Delta H_1 = 0, \quad (3)$$

have been calculated, and are plotted with the corresponding free energy quantity in fig. 7.

(For convenience in the following discussion the differences between the observed dilution functions and those given by eqn. (2) and (3) are called "excess" dilution functions.) From fig. 7 it is apparent that the "excess" entropy of dilution determines the sign of the "excess" free energy, and makes it positive despite the negative heat of dilution. Consequently the values of the parameter  $\chi$  in eqn. (1) are positive. In the agar-agar + water system at high polymer concentrations the negative "excess" entropy of dilution is numerically less than the exothermic heat of dilution, so that the "excess" free energy in this region is negative and gives negative values of  $\chi$ . No entropy or heat of dilution values

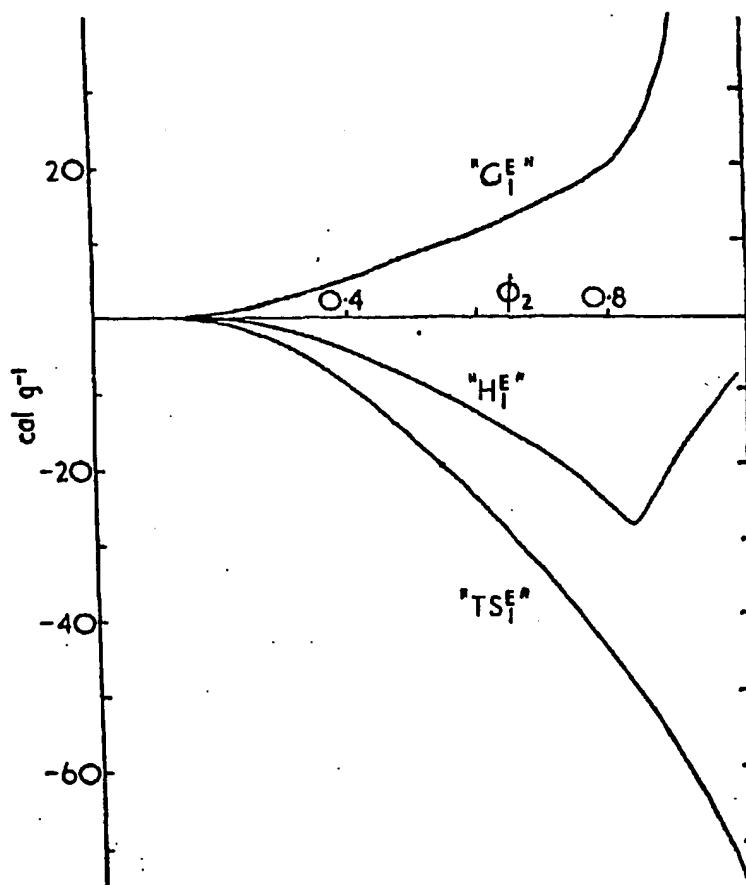


FIG. 7.—"Excess" thermodynamic dilution functions for the solution of polyethylene glycol 5000 (see text).  $G_1^E$  and  $TS_1^E$  at  $65^\circ C$ ,  $H_1^E$  at  $80.3^\circ C$ .

Fig. 7 reveals that the much greater increase in the value of  $\chi$  which was found in the region of high polymer concentration results from the sudden change in slope of the heat of dilution curve, which passes through a minimum. Similar behaviour in the heat of dilution is found in the dioxane + water system (fig. 3D) and in the ethanol + water system.<sup>7</sup> The vapour pressure results for the solution of polypropylene glycol suggest that the same behaviour is present there (fig. 3C).

The appearance of lower consolute temperatures in the solutions of the higher polyethylene glycols is another indication that negative entropies are determining the solution behaviour. Lower consolute temperatures have seldom been observed in polymer solutions.

The heat of mixing results in fig. 2 reveal marked differences in the behaviour of polymer molecules which seemingly differ only in chain length. It might reasonably have been anticipated that the dioxane curve would lie below that for the lowest polymer, since it contains only two ethylene oxide units. But the observed heats of mixing are in the same sequence as the proportions by weight of hydroxyl end groups in the various molecules, so that it seems probable that the end groups are responsible for the differences in behaviour. This hypothesis is supported by the results of some simple test-tube experiments with two related substances, ethylene glycol dimethyl ether and ethylene glycol monomethyl ether. The heat of mixing for the first of these substances, which contains no hydroxyl group, was positive for low water concentrations and became negative when the weight fraction of water reached 0.15. Addition of small quantities of water to the monomethyl ether resulted in a negative heat of mixing of a similar magnitude to that observed in the concentrated solutions of polyethylene glycol 300.

We wish to thank Prof. Gee for suggesting this work and for discussion of the results. We are grateful to Dr. A. J. Lowe of Oxirane for information concerning the polymers. One of us (G. N. M.) acknowledges with thanks the award of an Overseas Scholarship from New Zealand by the Royal Commission for the Exhibition of 1851.

## APPENDIX

### THE SYSTEM DIOXANE + WATER

(with A. Davis)

The vapour pressures of aqueous solutions of dioxane have been measured by Hovorka, Schaeffer and Dreisbach<sup>8</sup> (0-80° C), by Vierk<sup>9</sup> (25° C) and by Bacarella, Finch and Grunwald<sup>10</sup> (25° C). Vierk has also measured the heat of mixing at 20° C and Stallard and Amis<sup>11</sup> the heat capacity at 40° C. The densities have been measured, amongst others, by Hovorka, Schaeffer and Dreisbach and by Griffiths,<sup>12</sup> both of whom calculate the partial molar volumes at 25° C. These measurements show clearly that at room temperature this system has a positive excess Gibbs free energy, a negative excess enthalpy and a negative excess volume in mixtures weak in dioxane. This is the behaviour of solutions which show lower consolute points. We have therefore analysed these measurements further and have supplemented them with measurements of the vapour pressure up to 156° C and a search for such a consolute point up to 240° C.

PREVIOUS MEASUREMENTS.—We have disregarded the vapour pressures of Hovorka, Schaeffer and Dreisbach as their partial pressures at 25° C do not satisfy the Gibbs-Duhem equation and their total pressures are not in agreement with those of Bacarella, Finch and Grunwald. The partial pressures and activities of Vierk are satisfactory and lead to the excess free energy shown in fig. 8. The measurements of Bacarella, Finch and Grunwald are all at mole fractions of dioxane of less than 0.33. They give  $G^E$  about 3 % larger than that of Vierk.

The heat of mixing measured by Vierk at 20° C (fig. 8) has been confirmed by the three new measurements at 25° C reported below. The excess heat capacity of the system has been measured by Bacarella, Finch and Grunwald and is shown in fig. 9.

The densities of Hovorka and of Griffiths at 25° C agree and lead to the excess volume shown in fig. 10. Griffiths' measurements will not support the impossible discontinuities which he has reported in the partial molar volume at mole fractions of dioxane between 0.4 and 0.8.

FIG. 8.—Excess free-energy and enthalpy as a function of mole fraction of dioxane. Curve 1,  $GE$  from Vierk<sup>9</sup> (25° C); curve 2,  $GE$  from Bacarella, Finch and Grunwald<sup>10</sup> (25° C); curve 3,  $HE$  from Vierk<sup>9</sup> (20°) circles, and present measurements (25° C) triangles.

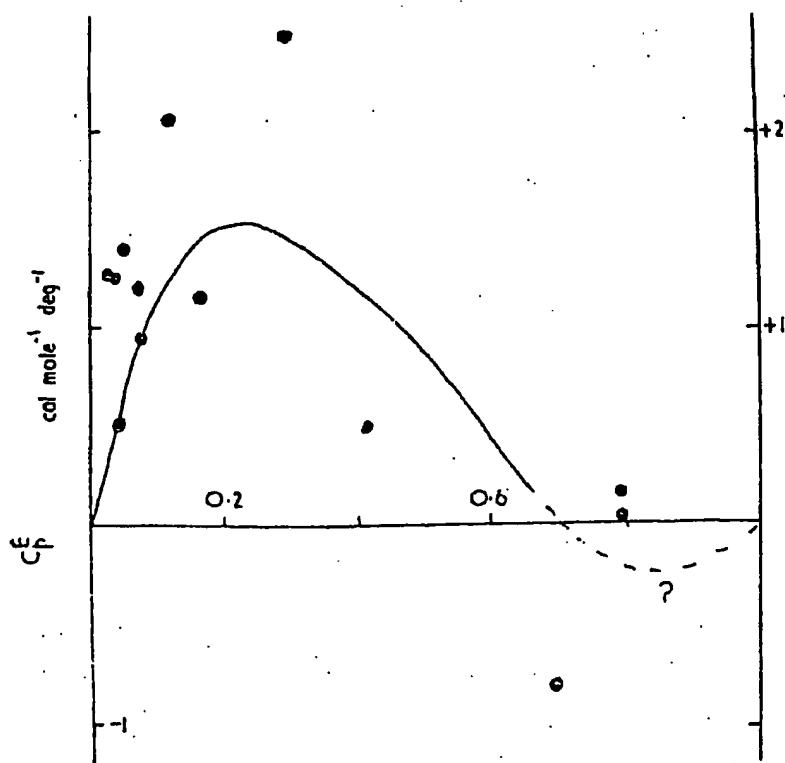
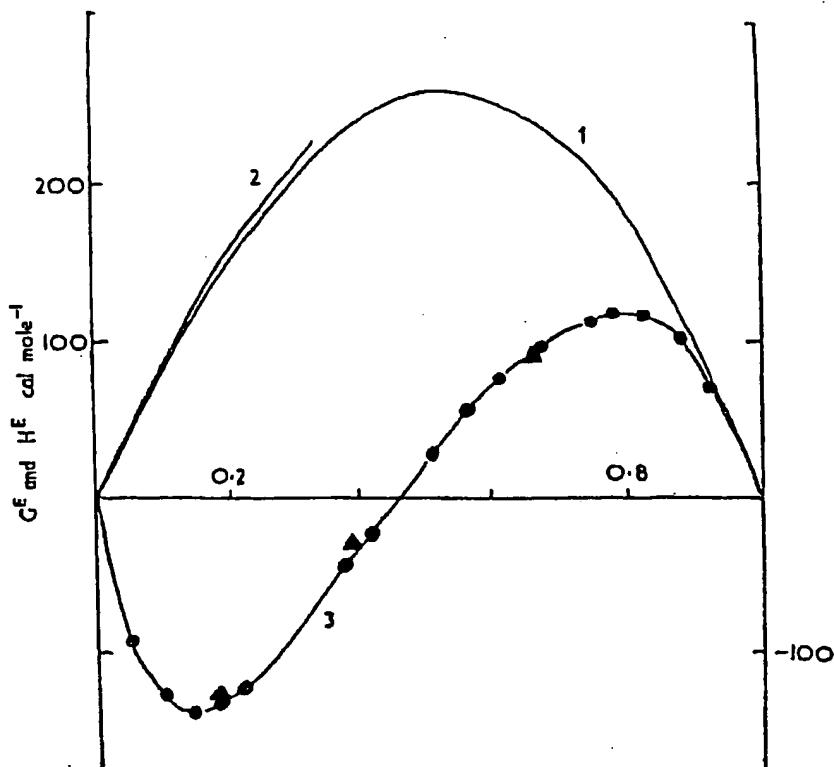


FIG. 9.—Excess heat capacity at 40° C as a function of the mole fraction of dioxane, from Stallard and Amis.<sup>11</sup>

PRESENT MEASUREMENTS.—A.R. dioxane was fractionally distilled and refluxed with liquid sodium. The dioxane was shown to be completely dry and free from all substances containing active hydrogen by the immediate formation of a coloured complex on adding a little fluorenone.<sup>13</sup> The dioxane, containing a small amount of complex in solution, was stored in *vacuo*. Mixtures were made up by weight by distillation of the de-gassed

## SOLUTIONS OF POLYETHYLENE GLYCOLS

The vapour pressures were measured by observing on a mercury manometer the pressure differences between the mixtures and pure water. Tubes containing the mixture and the water were heated in a vapour thermostat. The vapour pressures of water were those recommended by Dorsey.<sup>2</sup>

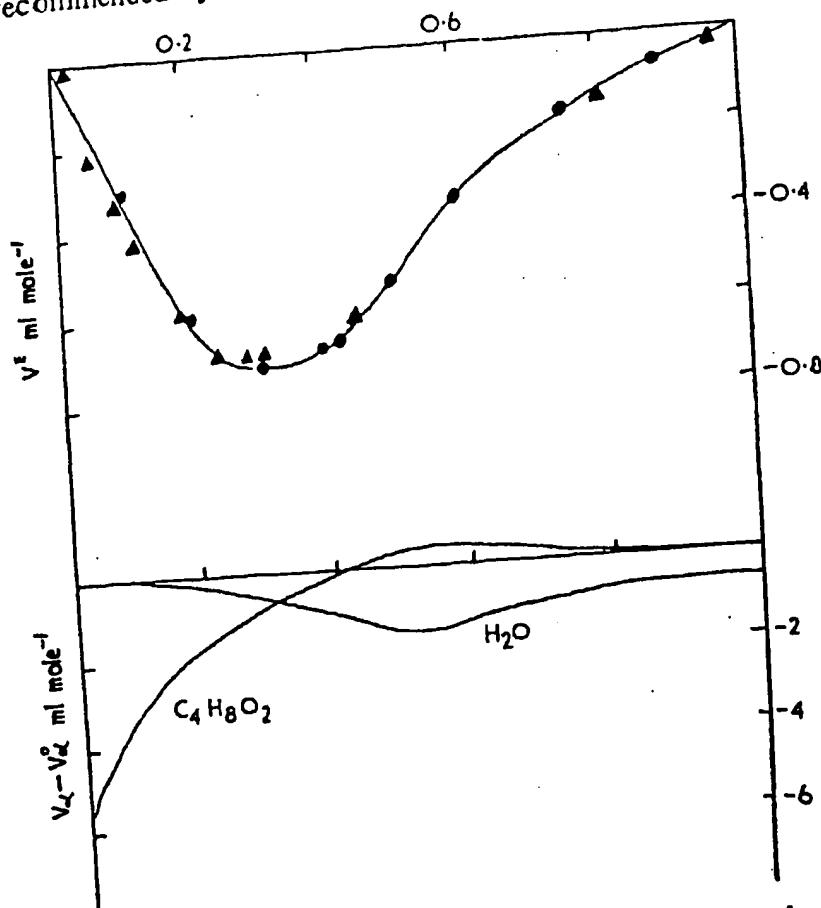


FIG. 10.—Excess volume at 25°C as a function of the mole fraction of dioxane, from Hovorka, Schaeffer and Dreisbach<sup>8</sup> (circles), and from Griffiths (triangles). Partial molar volumes from the curve for  $V^E$ .

The heats of mixing were measured in a U-tube calorimeter which has been described previously.<sup>14</sup>

TABLE 4.—VAPOUR PRESSURES IN mm Hg

mole fraction dioxane temp. °C	0.000	0.260	0.535	0.760	0.820	1.000
100	760	1138	1151	1110	1077	733
110	1075	1571	1581	1496	1462	986
120	1489	2130	2135	2001	1953	1304
130	2026	2837	2833	2628	2556	1696
140	2711	3722	3703	3390	3265	2174
150	3571	4808	4763	4300	4181	2752
156	4184	5556	5517	4927	4785	3156

The vapour pressure of pure dioxane can be approximately represented by

$$\log_{10} P \text{ (mm Hg)} = 7.72713 - 1813.98/(t^\circ \text{C} + 273.16)$$

with a maximum relative error (at 100°C) of 0.4 %. The observed boiling point was 101.2°C. These results agree with the measurements of Højendahl<sup>15</sup> within the error of  $\pm 2\%$  which he assigns to his results.

TABLE 5.—HEATS OF MIXING AT 25°C

mole fraction dioxane	0.175	0.388	0.601
$\Delta H$ (cal mole <sup>-1</sup> )	-130.5	-30.4	+70.2

Three mixtures of mole fraction of dioxane of 0.18, 0.39 and 0.60 were heated in evacuated sealed tubes to 240°C in a bath of glycerol. Neither opalescence nor the separation was observed.

## DISCUSSION

This system comes close to satisfying the conditions for a lower consolute point over the whole temperature range from 25 to 156° C. The excess free energy at 25° C is shown in fig. 8, and two estimates of that at 150° C in fig. 11. One of these estimates is based on the observed vapour pressures but with no correction for the deviations from the perfect gas laws. These deviations will be large but their relative effect on  $GE$  is probably not

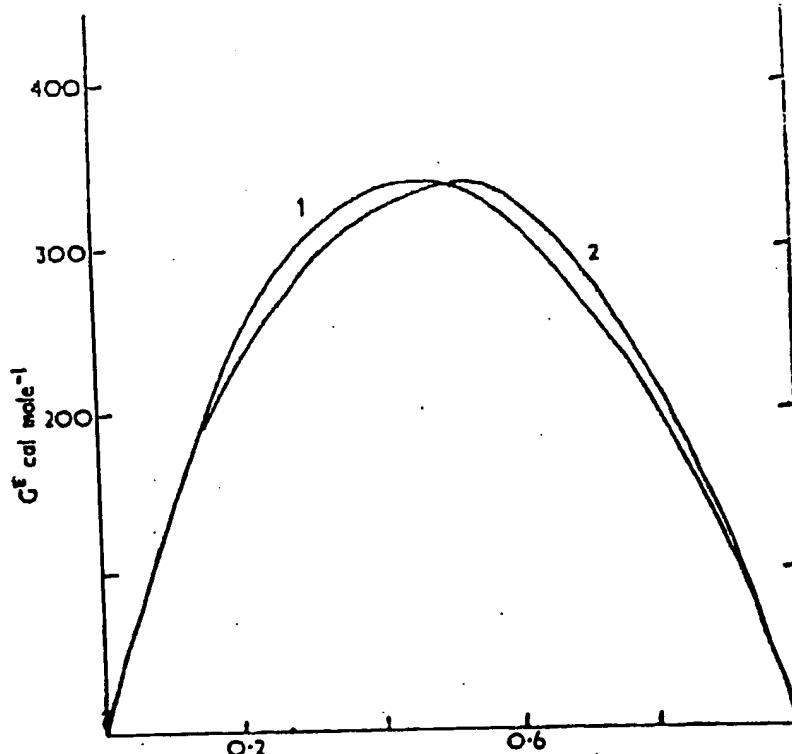


FIG. 11.—Estimates of  $GE$  at 150° C from (1) vapour pressures at 150° C and (2) from  $HE$ ,  $SE$  and  $C_p E$  at lower temperatures (see text).

serious owing to its unusually large size. The second estimate is a calculation from  $HE$  and  $TSE$  at 25° C and  $C_p E$  at 40° C with the additional assumption that  $C_p E$  is independent of temperature. The agreement between the two estimates is remarkably good. It is found that  $GE$  is about 10 % too small for curves of these shapes, at both 25 and 150° C for the system to show a consolute point. This is in agreement with direct observation. The nearness of the system to phase separation is shown by the readiness with which this occurs in the presence of an electrolyte. For example, as little as 0.005 (mole fraction) of HCl causes phase separation at room temperature.<sup>16</sup>

A comparison of the properties of this system with solutions of polyethylene glycols is made in the body of this paper.

<sup>1</sup> Taylor and Rowlinson, *Trans. Faraday Soc.*, 1955, **51**, 1183.

<sup>2</sup> Dorsey, *Properties of Ordinary Water Substance* (Reinhold, N.Y., 1940).

<sup>3</sup> Beynon and Humphries, *Trans. Faraday Soc.*, 1955, **51**, 1065.

<sup>4</sup> Coffin, Devins, Dingle, Greenblatt, Ingraham and Schrage, *Can. J. Res. B*, 1950, **28**, 579.

<sup>5</sup> Baughan, Jones and Stewart, *Proc. Roy. Soc. A*, 1954, **225**, 478.

<sup>6</sup> Gee, *Quart. Rev.*, 1947, **1**, 282. Friche and Lüke, *Z. Elektrochem.*, 1930, **36**, 309.

<sup>7</sup> Prigogine and Defay, *Chemical Thermodynamics* (Longmans, London, 1954), p. 431.

<sup>8</sup> Hovorka, Schaeffer and Dreisbach, *J. Amer. Chem. Soc.*, 1936, **58**, 2264.

<sup>9</sup> Vierk, *Z. anorg. Chem.*, 1950, **261**, 283.

<sup>10</sup> Bacarella, Finch and Grunwald, *J. Physic. Chem.*, 1956, **60**, 573.

<sup>11</sup> Stallard and Amis, *J. Amer. Chem. Soc.*, 1952, **74**, 1781.

<sup>12</sup> Griffiths, *J. Chem. Soc.*, 1952, 1326; 1954, 860.

<sup>13</sup> Morantz and Warhurst, *Trans. Faraday Soc.*, 1955, **51**, 1375.

<sup>14</sup> Thacker and Rowlinson, *Trans. Faraday Soc.*, 1954, **50**, 1036.

<sup>15</sup> Højendahl, *Danske Vid. Selsk. Mat.-Fys. Medd.*, 1946, **24**, no. 2.

## Polypropylene Glycols (PPGs)

### Overview

Polypropylene glycols are polymers of propylene oxide. They are clear, viscous liquids with low pour points. Viscosity increases and water solubility decreases with increasing molecular weight.

PPGs can be blended to obtain liquids with intermediate viscosities. The molecular weights range from low for water-soluble to high for water-insoluble applications.

### Properties

Series	INCI/CTFA Nomenclature	Average Molecular Weight	Specific Gravity <sup>1</sup>	Average Viscosity <sup>2</sup>			Flash Point <sup>3</sup>	Average Pour Point <sup>4</sup>	Cloud Point <sup>5</sup>		Refractive Index <sup>7</sup>
Units			25/25°C	25°C	40°C	100°C	PMCC	°C	1% aqueous solvent <sup>6</sup>	°C	
P400E	PPG-12	425	1.007	68	31	5	>150	-49	>95	69	1.445
P600E	PPG-15	600	1.003	84	38	6	227	-47	65	57	1.4465
P1000E	PPG-17	1000	1.003	143	71	11	>150	-43	21	38	1.447
P1200E	PPG-20	1200	1.003	160	80	13	174	-41	20	32	1.448
P2000E	PPG-26	2000	1.002	230	143	24	198	-31	15	20	1.449
P4000E	PPG-34	4000	1.004	1110	438	73	185	-20	9	10	1.450

#### Test Methods:

<sup>1</sup> Specific Gravity: ASTM D 892

<sup>2</sup> Viscosity: ASTM D 445

<sup>3</sup> Flash Point: ASTM D 92

<sup>4</sup> Pour Point: ASTM D 97

<sup>5</sup> Cloud Points: ASTM D 2024

<sup>6</sup> 10% surfactant in a solution of 25% Diethylene glycol butyl ether in water.

<sup>7</sup> Refractive Index: ASTM D 1218

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